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**Supporting information for article:**

**Time-resolved X-ray absorption spectroelectrochemistry of redox active species in solution**

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## S1. Experimental section

$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{FeCl}_2$  and  $\text{KCl}$  were purchased from Aldrich and TCI and were used without purification. De-ionized water was used as solvent. The 3D-printed XAS-spectroelectrochemical cell was designed using the solidworks® software and produced on a Stratasys Objet 30 Pro 3D printer with Veroclear® or Verowhite® printing materials.

## S2. XAS data collection and analysis

X-ray absorption spectra were collected at the ROCK beamline of SOLEIL, at a ring energy of 2.75 GeV and a current of 500 mA. A Si111 double crystal quick-XAS monochromator oscillating at a 2 Hz frequency was used to collect time-resolved data. The incoming ( $I_0$ ) and transmitted ( $I_1$ ) beam intensities were monitored using  $\text{N}_2$ -filled ionization chambers. A reference spectrum was constantly measured by placing an Fe foil between the  $I_1$  and  $I_2$  ionization chambers. Quick-XAS spectra were extracted and reduced using a home-made software. The Athena software was used to normalize and average reduced spectra and to perform linear combination fittings.

## S3. Electrochemistry

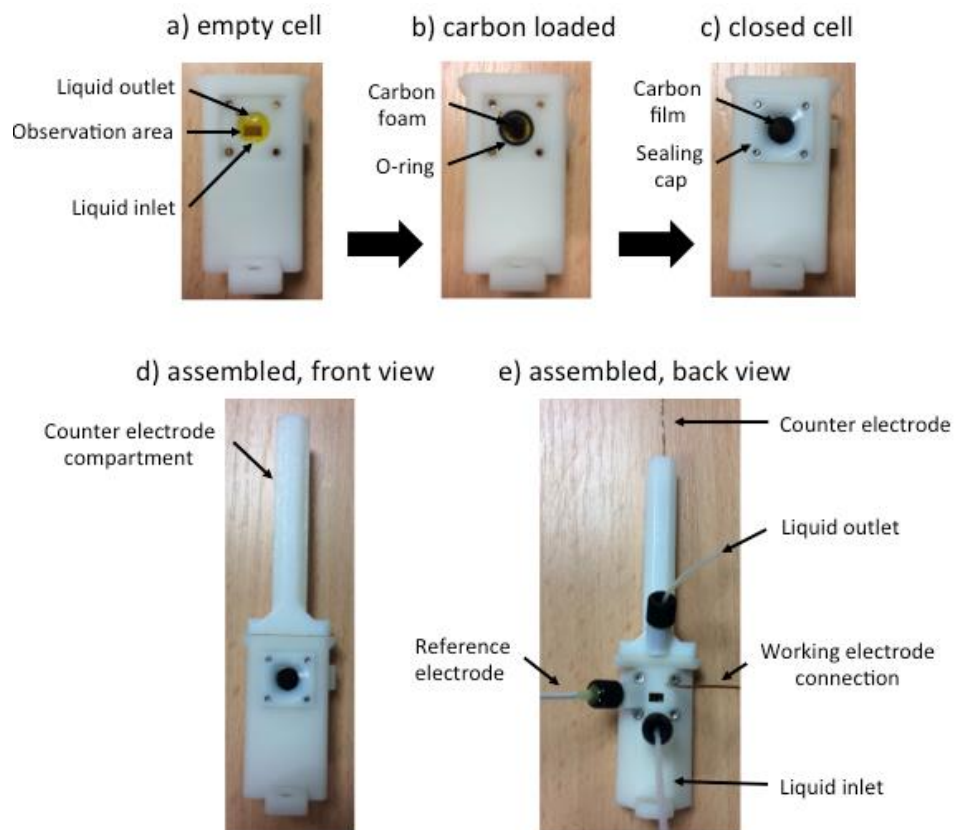
### S3.1. Conventional electrochemistry

All electrochemical experiments were performed under an argon atmosphere. Cyclic voltammetry measurements were recorded using an Autolab potentiostat controlled with the Nova 1.10 software or a Bio-logic potentiostat controlled with the EC-lab software. The counter electrode (CE) used was a platinum wire and the working electrode (WE) was a glassy carbon (3mm diameter, 7 mm<sup>2</sup>) disk polished before each voltamogram with 1 μm diamond paste, sonicated in an ethanol bath, and washed with ethanol and water. The reference electrode (RE) used was a Pt wire or a saturated calomel electrode (SCE) isolated from the rest of the solution by a fritted bridge. Experiments were performed in de-ionized water using 0.1 M potassium chloride as supporting electrolyte.

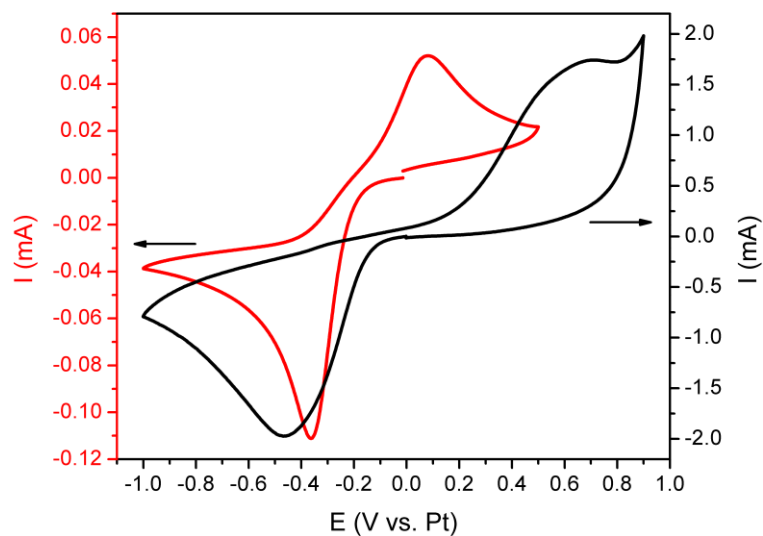
### S3.2. Electrochemistry in the XAS-spectroelectrochemical cell

Cyclic voltammetry measurements were recorded using a Bio-Logic potentiostat controlled by EC-Lab 1.10 software package. The counter electrode used was a platinum mesh and the working electrode was a carbon foam contacted by a glassy carbon square film (60 μm thick and 10 mm<sup>2</sup> large). The pseudo reference electrode used was a Pt wire inserted into the analysis chamber. Experiments were performed in de-ionized water using 0.1 M potassium chloride as supporting electrolyte. A volume of 3 ml of 20 mM aqueous solution of  $\text{Fe}^{\text{III}}\text{Cl}_3 \cdot 6\text{H}_2\text{O}$  with 0.1M  $\text{KCl}$  electrolyte, was degassed with argon for 10 min. The analysis chamber was filled from the bottom to the top using a peristaltic pump. The whole system

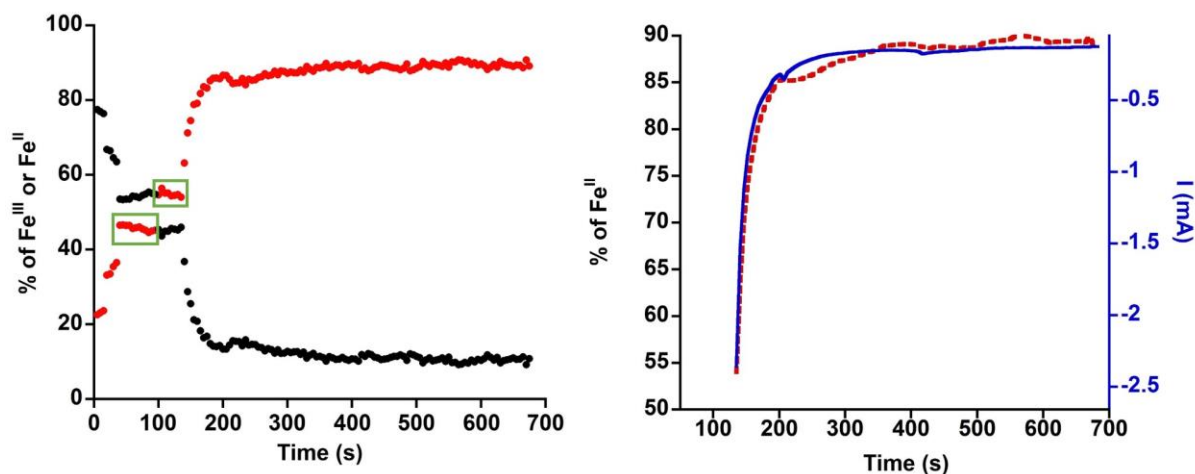
was kept under argon atmosphere during the measurements. The same procedure was used for the aqueous solution of  $\text{Fe}^{\text{II}}\text{Cl}_2$ , with the only exception that the solution was prepared under argon atmosphere in order to prevent the aerobic oxidation of the ferrous ions.



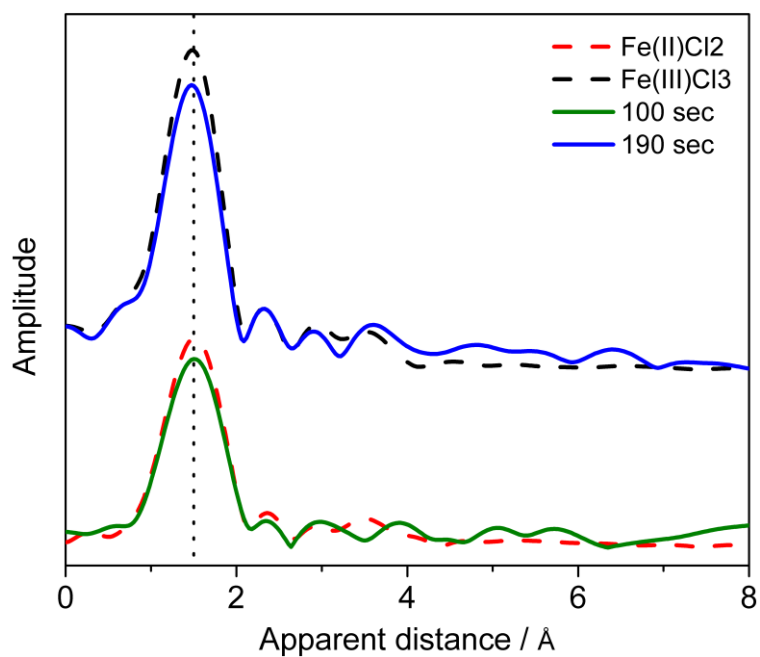
**Figure S1** Front (a, b, c, d) and back (e) views of the XAS cell at different stages of its assembly.



**Figure S2** CV of 20 mM  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  aqueous solution in presence of 0.1M KCl recorded in the 3D printed XAS cell at 20 mV/s with glassy carbon film and carbon foam as WE, Pt mesh as CE and Pt wire as a pseudo reference (black line). CV of 20 mM  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  aqueous solution in presence of 0.1M KCl recorded in a conventional electrochemical cell at 20 mV/s using a glassy carbon disk ( $7 \text{ mm}^2$ ) as a WE, Pt mesh as a CE and Pt as a RE (red line). The potential shift in the presence of the foam as WE is due to the irreversible behavior of the redox process with an inner electron transfer mechanism previously reported by Tanimoto *et al.* (Tanimoto & Ichimura, 2013).



**Figure S3** XANES *in situ* monitoring of Fe(II) (red dots) and Fe(III) (black dots) proportions (%) during a CPE of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (20 mM) aqueous solution in presence of 0.1M KCl using a glassy carbon foam as a WE, Pt mesh CE and Pt wire as a pseudo reference (left). The green rectangles correspond to two periods of 60 and 40 s when the potential was stopped while XAS spectra were collected in order to check for radiation damage. Overlay of the *in situ* XANES spectroscopic monitoring of Fe(II) formation (red dashed line) and electrochemical measurement of the current (blue line) during the last 550 s of the CPE at -0.8 V vs. Pt (right).



**Figure S4** Fourier transform EXAFS spectra ( $k$  range =  $2.5\text{--}8\text{ \AA}^{-1}$ ) of reference  $\text{FeCl}_3\cdot 6\text{H}_2\text{O}$  (black dashed line) and  $\text{Fe}^{\text{II}}\text{Cl}_2$  (red dashed line) solutions and of time-resolved points taken after 100 (green plain line) and 190 (blue plain line) seconds.